

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2002-240215**

(43)Date of publication of
application : **28.08.2002**

(51)Int.Cl.

B32B 27/32
B01D 69/12
B01D 71/26
B32B 5/32
C08J 9/36
H01M 2/16
// C08L 23:00

(21)Application
number : **2001-046477**

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(22)Date of filing : **22.02.2001**

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(54) COMPOSITE FILM AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a composite film usable as a separator of a very high quality in a field of a chemical battery like a lithium battery and usable as a filtering filter remarkably improved in a filtering speed or the like, having good wettability even in a field of a separation membrane, and a method for manufacturing the same.

SOLUTION: The composite film comprises a coating layer made of a porous material (B) of a functional polymer substance capable of being gelatinized on at least one surface of a polyolefin fine porous film (A) so that a mean particle size of the material (B) is larger than a maximum pore size of the porous film (A). The method for manufacturing the composite film comprises a step of coating the functional polymer substance solution on at least one surface of the polyolefin fine porous film (A), a step of phase separating the coating surface by contacting the coating surface with a poor solvent of the functional polymer substance, and a step of forming the coating layer made of the porous material (B) of the functional polymer substance by heating and drying the phase separated surface.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention about bipolar membrane and a manufacturing method for the same in more detail, Electrolysis solution pouring nature [in / in the field of a chemical cell like a lithium cell / a battery construction process], Or there is no inconvenience by gap between the members forming in repetition charge and discharge, a crevice, etc., It can be used as a very quality separator which can also reduce interfacial resistance, and further, wettability with the drug solution which serves as a candidate for separation also in the field of a demarcation membrane is good, therefore it is related with bipolar membrane which can be used as a barrier filter in which filtration velocity etc. have been improved remarkably, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]Various porous membrane is developed conventionally and it is used as a separator of a filter, an electrolysis film, and a nonaqueous solvent type cell. Especially in the field of a lithium secondary battery and a lithium ion battery, In a cell or a use device since the reactant high active material is used, Also in the separator which separates an anode and a negative electrode as one means for various kinds of safeguards being formed and preventing generation of heat of a cell, ignition, or a burst accident by the short circuit of an external circuit, a surcharge, etc., With the function to suspend the cell reaction to which it was blockaded by generation of heat at the time of abnormalities, and the hole of the polyethylene used and the fine porous membrane made from polypropylene led the separator. Even if it becomes an elevated temperature, the shape as a separator is maintained, and it is required that it should have a function in which a positive pole substance and a negative-electrode substance prevent the dangerous situation which carries out a direct reaction. The separator with the film shape maintenance characteristic low [the separator of fine porosity manufactured by extension used widely now] in an elevated temperature and the big film shape maintenance characteristic in an elevated temperature was called for.

[0003]On the other hand, although polyolefin fine porous membrane has been used from the former also in the field of a demarcation membrane taking advantage of the micropore structure which is the characteristic as demarcation membranes, such as gas separating, liquid-liquid separation, and solid-liquid part difficulty, In uses demanded, such as solvent resistance to which importance has come to be attached by separating operation in recent years, and chemical resistance, there is a field which cannot show sufficient tolerance with isolation maintained, and the request was increasing that the performance of the polyolefin fine porous membrane as a demarcation membrane should be improved.

[0004]In order to cancel the problem which such conventional polyolefin fine porous membrane has, the trial of former versatility was made and the examination which laminates other resin layers on it by using polyolefin fine porous membrane as a substrate as one, and is used as bipolar membrane was also made, but. Neither was able to say that the purpose was fully attained in respect of intensity or functionality.

[0005]For example, the porous membrane which consists of ultra high molecular weight polyethylene, and an outer layer as a separator which the obstructiveness in low temperature is high and has the film shape maintenance characteristic in an elevated temperature in JP,7-22014,A with polyethylene.

Although the separator with the big elevated-temperature film shape maintenance characteristic of having used from the nonwoven fabric containing the multilayer textiles which a green sand core becomes from resin whose melting point is higher than polyethylene not less than 20 °C was proposed, it was not able to be said that it was enough in the field of the function currently called for, for example, the field of the characteristic in an elevated temperature, or safety. To one field of the porous fluoro resin film fibrillated by stretching treatment in JP,9-161756,A. Although the porous membrane which consists of ultra high molecular weight polyethylene or high density polyethylene was laminated and the separator which provided high-density-polyethylene porous membrane in the field of another side was proposed, the thing of sufficient characteristic was not able to say like the above-mentioned case.

[0006]In order to expand the performance as a separator for cells and the performance as a demarcation membrane which polyolefin fine porous membrane has and to raise them in recent years under such a situation, It is anxious for development of bipolar membrane in which the porosity enveloping layer which consists of other functional polymer substances was formed on polyolefin fine porous membrane, and a manufacturing method for the same.

[0007]

[Problem(s) to be Solved by the Invention]In the field of a chemical cell like a lithium cell, the technical problem of this invention, Gap between the members forming in the electrolysis solution pouring nature in a battery construction process, or repetition charge and discharge, There is no inconvenience by a crevice etc. and it can be used as a very quality separator which interfacial resistance can also reduce, Also in the field of a demarcation membrane, wettability with the drug solution used as the candidate for separation is good, therefore there is in providing bipolar membrane which can be used as a barrier filter in which filtration velocity etc. have been improved remarkably, and a manufacturing method for the same.

[0008]

[Means for Solving the Problem]In bipolar membrane which forms an enveloping layer which consists of a porous body of a functional polymer substance gelable to the 1st [at least] page of polyolefin fine porous membrane as a result of repeating research wholeheartedly, in order that this invention persons may solve an aforementioned problem, When an average pore size of a porous body was adjusted to a specific range, it finds out that bipolar membrane which can be used also as a demarcation membrane also as a quality separator for cells which is not in the former is obtained, and came to complete this invention.

[0009]Namely, in bipolar membrane which forms an enveloping layer which consists of a porous body (B) of a functional polymer substance gelable to the 1st [at least] page of polyolefin fine porous membrane (A) according to the invention of the 1st of this invention, Bipolar membrane, wherein an average pore size of a porous body (B) is larger than the maximum aperture of polyolefin fine porous

membrane (A) is provided.

[0010]According to the invention of the 2nd of this invention, in the 1st invention, bipolar membrane, wherein thickness is 1.01 times - 10 times the polyolefin fine porous membrane (A) and air permeability is 1.01 times - 10 times the polyolefin fine porous membrane (A) is provided.

[0011]A process of applying a functional polymer substance solution to the 1st [at least] page of polyolefin fine porous membrane (A) according to the invention of the 3rd of this invention, A process which carries out phase separation by contacting this spreading side to a poor solvent of this functional polymer substance, The 1st or 2nd invention consisting of a process in which an enveloping layer which consists of a porous body (B) of a functional polymer substance is made to form is provided with a manufacturing method of bipolar membrane of a statement by heating and drying this field that carried out phase separation.

[0012]A process of applying to the 1st [at least] page of polyolefin fine porous membrane (A) a solution which dissolved a functional polymer substance in a mixture of the good solvent and poor solvent according to the invention of the 4th of this invention, A process which carries out phase separation by carrying out evaporation scattering of the good solvent selectively from this spreading side, The 1st or 2nd invention consisting of a process in which an enveloping layer which consists of a porous body (B) of a functional polymer substance is made to form is provided with a manufacturing method of bipolar membrane of a statement by removing a poor solvent which remains to this field that carried out phase separation.

[0013]A process of applying a functional polymer substance solution to the 1st [at least] page of polyolefin fine porous membrane (A) according to the invention of the 5th of this invention, The 1st or 2nd invention consisting of a process in which a process which carries out phase separation, and an enveloping layer which consists of a porous body (B) of a functional polymer substance by heating and drying this field that carried out phase separation are made to form is provided with a manufacturing method of bipolar membrane of a statement by making this spreading side cool.

[0014]This invention relates to bipolar membrane and a manufacturing method for the same, as mentioned above, but what is shown below is included as the desirable mode.

(1) The bipolar membrane according to claim 1 or 2, wherein polyolefines used for polyolefin fine porous membrane (A) are weight-average-molecular-weight 1×10^6 - 15×10^6 .

(2) Said bipolar membrane, wherein the weight average molecular weight/number average molecular weight (Mw/Mn) of polyolefine used for polyolefin fine porous membrane (A) or a polyolefin composition are 5-300.

(3) Said bipolar membrane, wherein polyolefine used for polyolefine or a polyolefin composition used for polyolefin fine porous membrane (A) is polypropylene or polyethylene.

(4) Said bipolar membrane which is a polyolefin composition in which polyolefine used for polyolefin fine porous membrane (A) contains with a weight average molecular weight of 500,000 or more polyolefine.

(5) A polyolefin composition containing the with a weight average molecular weight of 500,000 or more polyolefine used for polyolefin fine porous membrane (A), Said bipolar membrane being a constituent which consists of with a weight average molecular weight of 500,000 or more super-polymers tatami polyethylene and with an or more 10,000 weight average molecular weight [less than 500,000] high density polyethylene.

(6) Polyolefin fine porous membrane. A polyolefin composition containing the with a weight average

molecular weight of 500,000 or more polyolefine used for (A) with a . weight average molecular weight of 500,000 or more ultra high molecular weight polyethylene, with an or more 10,000 weight average molecular weight [less than 500,000] high density polyethylene, and a shutdown function. Consist of polyolefine to give and, on the other hand, polyolefine which gives this shutdown function, Said bipolar membrane being at least one sort chosen from ethylene-alpha olefin copolymers manufactured using low density polyethylene, linear low density polyethylene, low molecular weight polyethylene of the molecular weights 1000-4000, or a single site catalyst.

(7) Said bipolar membrane, wherein air permeability of polyolefin fine porous membrane (A) is 800 or less seconds/100 cc.

(8) Said bipolar membrane to which tensile strength of polyolefin fine porous membrane (A) is characterized by **** intensity being 3000 mN(s)/not less than 25 micrometers by 80 or more MPa.

(9) Said bipolar membrane, wherein a functional polymer substance which constitutes a porous body (B) carries out copolymerization of the monomer of polyacrylonitrile, polyvinylidene fluoride, a polyoxyethylene, polyoxypropylene, or these polymer.

(10) Said bipolar membrane, wherein the maximum aperture of a porous body (B) is 1 micrometers or more.

[0015]

[Embodiment of the Invention]Hereafter, bipolar membrane of this invention and a manufacturing method for the same are explained in detail.

[0016]1. Polyolefin fine porous membrane (A)

The polyolefin fine porous membrane in particular used as a substrate of the bipolar membrane of this invention is not limited, and as long as it is publicly known, it may be based on what kind of process of what kind of construction material. As polyolefine used for polyolefin fine porous membrane, the crystalline homopolymer or copolymer which polymerized ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, etc. is mentioned. Although these homopolymers or copolymers can be alone used in that case, two or more sorts of things may be blended and used.

[0017]In these, from the plasticity of fine porosity, a viewpoint of a mechanical strength, etc. The amount polyethylene of polymers, especially weight average molecular weight contain the thing used as 1×10^6 - 15×10^6 , and high-density ultra high molecular weight polyethylene of 5-300 has preferred weight average molecular weight/number average molecular weight (Mw/Mn). Such polyethylene may be any of a simple substance or a constituent.

[0018]Here, as a desirable mode which blends two or more sorts of polyolefines, there is a constituent which consists of with a weight average molecular weight of 500,000 or more super-polymers tatami polyethylene and with an or more 10,000 weight average molecular weight [less than 500,000] high density polyethylene. As the 3rd polyolefin component that can give a shutdown function further into this constituent in that case, At least one sort of polyolefines chosen from the ethylene-alpha olefin copolymers manufactured using low density polyethylene, linear low density polyethylene, low molecular weight polyethylene of the molecular weights 1000-4000, or a single site catalyst may be blended.

[0019]The manufacturing method of polyolefin fine porous membrane, Although not limited, in weight average molecular weight, 5×10^5 - 2.5×10^6 , and weight average molecular weight/number average molecular weight, for example 5 to 50 % of the weight of less than ten polyolefines, Prepare the solution which consists of 95 to 50 % of the weight of solvents, and this solution is extruded from a die, It is

preferred to use the polyolefin fine porous membrane manufactured by cooling, forming a gel composition, extending this gel composition at temperature with a melting point of +10 °C or less of polyolefine, and removing a residual solvent after an appropriate time.

[0020]As polyolefin fine porous membrane used for this invention, In a void content, the air permeability in 25 micrometers of thickness 30 to 95% Usually, 2000 or less seconds/100 cc. The fine porous membrane in which 0.005-1 micrometer and tensile breaking strength have 100 or more MPa, and **** intensity has 80 or more MPa of mechanical physical properties [3000 or more mN of] of 5500 or more mN preferably in 800 or less seconds/100 cc and the diameter of an average breakthrough is desirable.

[0021]Although the thickness of polyolefin fine porous membrane is chosen suitably, it is usually about 1-25 micrometers preferably 0.1-50 micrometers. It is difficult for thickness to present practical use from the shortage of a mechanical strength of a film in less than 0.1 micrometer, and if it exceeds 50 micrometers, effective resistance becomes large too much and is not preferred.

[0022]2. Porous body (B)

The porous body (B) in particular of the gelable functional polymer substance used as an enveloping layer of the bipolar membrane of this invention is not limited, and as long as it is publicly known, it may be based on what kind of process of what kind of construction material.

[0023]Although various publicly known resin is mentioned as a functional polymer substance which constitutes a porous body, For example, when using the bipolar membrane of this invention for separators for cells, such as a lithium cell, Since it needs to be stable also to an electrolysis solution or a cell reaction and it is moreover necessary to be low penetration resistance compared with penetration resistance of polyolefine mark porous membrane, while it has compatibility to an electrolysis solution, Polyvinylidene fluoride, polyacrylic nitril, polyvinyl chloride, etc. other than polyether, polyester, polyamine, and polysulfide are preferred. In that case, a straight-chain-shape polymer independent may be sufficient, and these are made to postpolymerize by methods, such as heating, in the state of a monomer, oligomer, or a prepolymer, and are good also as a bridging body.

[0024]Especially in these performance polymers, the polyvinylidene fluoride from viewpoints of the performance as the separator for cells or a demarcation membrane, a mechanical strength, etc., polyacrylic nitril, polyether (a polyoxyethylene, polyoxypropylene), etc. are preferred.

[0025]As a method of making the enveloping layer which consists of a porous body of the above-mentioned functional polymer substance forming in the surface of at least one of the two of polyolefine mark porous membrane, Although a phase separation method, an extraction method, the extending method, the charged particle glaring method, etc. which are processes generally used to the process of a demarcation membrane although not restricted in particular can be used, It is not preferred to do damage to polyolefine mark porous membrane by the morphosis, or to check the characteristic of polyolefine mark porous membrane by the formation. Then, as a method which does not spoil the mechanical property or the substance penetration characteristic of polyolefine mark porous membrane without chemicals degradation or radiation deterioration, without exposing to temperature which exceeds the melting point of polyolefine, For example, the porosity-ized method of a polymeric material as shown in the following (a) - (c) can use selectively. namely[0026](a) How to manufacture the bipolar membrane which had the surface covered with a porous polymeric material at least by drying after carrying out phase separation by applying to the surface of at least one of the two of polyolefin fine porous membrane the polymeric material which dissolved in the good solvent, and making a poor solvent

contact.

(b) The polymeric material which dissolved in the partially aromatic solvent of a good solvent and a poor solvent is applied to the surface of at least one of the two of polyolefine mark porous membrane, How to manufacture the bipolar membrane which had the surface covered with a porous polymeric material at least by removing the solvent which remains after carrying out phase separation, when a good solvent carries out evaporation scattering selectively.

(c) How to manufacture the bipolar membrane which had the surface covered with a porous polymeric material at least by drying after applying to the surface of at least one of the two of polyolefine mark porous membrane the polymeric material which dissolved in the good solvent and carrying out phase separation by cooling.

[0027]Spreading of the polymeric material in (a) - (c) in that case, Usually, it is carried out by conventional flow casting or coating method, for example, a roll coater, an air knife coating machine, braid coating machine, rod coating machine, bar coating machine, comma coating machine, photogravure coating machine, silk screen coating machine, die coater, the micro photogravure coating-machine method, etc.

[0028]Although the content of the polymeric material in coating liquid is suitably adjusted with a coating method and the thickness of a thin film which should be formed, it is usually 1 to 10 % of the weight. As a solvent of the above-mentioned coating liquid, as shown below, according to the material of performance polymers, it is chosen suitably.

[0029]For example, in the case of polyvinylidene fluoride, as a good solvent, Cyclohexanone, gamma-butyrolactone, ethylene carbonate, dimethylacetamide, N-methyl pyrrolidone, dimethyl sulfoxide, etc. are mentioned, and, on the other hand, benzene, methyl isobutyl ketone, dimethylformamide, etc. are mentioned as a poor solvent. In the case of polyacrylic nitril, as a good solvent, A phenylenediamine, N-formyl hexamethyl amine, N-nitrosopiperidine, Maleic anhydride, acetic anhydride, gamma-butyrolactone, and dioxan, an ethylene oxalate, Ethylene carbonate, 2-oxazolidone, a 1-methyl-2-pyrrolidone, Epsilon caprolactam, dimethylformamide, a 2-methyl-beta-cyanoethylformamide, The cyanoacetic-acid, dimethylacetamide, N, and N-dimethyl- alpha and alpha, alpha-trifluoroacetamide, Hydronaliumacetonitrile, chloromethyl cyanid, MARONI tolyl, fumaronitrile, Bis(2-cyanoethyl)ether, a bis(4-cyanobutyl)sulfone, 1,3,3,5-tetracyano pentane, nitromethane/water (94/6) (a weight section/ weight section), 1,1,1-trichloro-3-nitro 2-propane, 3-nitrophenol, Methylthio JIANETO, dimethyl sulfoxide, a tetramethylen sulfoxide, 2-hydroxyethyl methylsulfone, dimethyl phosphite, p-phenolsulfonic acid, etc. are mentioned, and, on the other hand, as a poor solvent Alcohols, such as methanol and ethanol, Ketone, such as diethylether and methyl ethyl ketone, a 1,6-hexanediamine, **** propyl, a formamide, N.N-dimethylformamide, a diethylformamide, A dimethyloxamide, acetonitrile, acrylonitrile, 1-hydroxypropione nitril, methylthio JIANETO, hexamethylene dithiocyanate, 1-nitrophenol, diethyl sulfoxide, diethyl sulfone, a 3,4-dimethylsulfone, etc. are mentioned. A polyoxyethylene case as a good solvent, Alcohols, such as benzene, chloroform, methanol, and ethanol, cyclohexanone, N.N-dimethylformamide, acetonitrile, etc. are mentioned, and, on the other hand, ether agents, such as wood ether and diethylether, dioxane, etc. are mentioned as a poor solvent.

[0030]As for heat treating time, although the coat obtained by spreading is usually dried by heat treatment, the range of this heat treatment temperature is 60-90 **, and it is preferred that it is a range for 1 to 10 minutes.

[0031]Thus, although the thickness of the enveloping layer which consists of porous bodies formed in at

least one field of polyolefin fine porous membrane changes also with the apertures and void contents of polyolefin fine porous membrane, it is usually 0.001-50 micrometers. Since it becomes impossible to disregard substance penetration resistance when it becomes difficult to avoid generating of a defect if there is less thickness of an enveloping layer than 0.001 micrometer and it exceeds 50 micrometers on the other hand, it is not desirable.

[0032]The place of the bipolar membrane of this invention by which it is characterized most is at the point that the average pore size of a porous body (B) must be larger than the maximum aperture of polyolefin fine porous membrane (A). If this requirement has an important meaning technically, this requirement is satisfied by this invention and this requirement will not be satisfied to becoming possible to grant a desired function to bipolar membrane, without causing big increase of substance penetration resistance, substance penetration resistance becomes large and the purpose cannot be attained. By the way, 0.1 micrometers or more in the maximum aperture of the porous body which constitutes an enveloping layer is usually 1 micrometers or more preferably.

[0033]3. The bipolar membrane which is more than bipolar membrane and was produced by making, Since the problem is corrected maintaining the characteristic of the polyolefin fine porous membrane itself by providing the enveloping layer which becomes at least one side of polyolefin fine porous membrane (A) from the porous body (B) of a functional polymer substance, In the field of rechargeable batteries, such as a nickel hydride battery, a nickel-cadmium battery, a nickel zinc carbon cell, a silver-zinc carbon cell, a lithium secondary battery, and a lithium polymer rechargeable battery, Gap between the members forming in the electrolysis solution pouring nature in a battery construction process, or repetition charge and discharge, It not only can use it as a very quality separator which there is no inconvenience by a crevice etc. and interfacial resistance can also reduce, but further, Also in the field of a demarcation membrane, wettability with the drug solution used as the candidate for separation is good, therefore it can be effectively used also as a barrier filter in which filtration velocity etc. have been improved remarkably.

[0034]Although the thickness of the bipolar membrane of this invention changes a little with usage, objects, etc., Usually, it is desirable that they are 1.05 to 5 times preferably 1.01 to 10 times of the polyolefin fine porous membrane used as a substrate, and, also as for the air permeability, on the other hand, it is desirable that they are 1.05 to 5 times preferably 1.01 to 10 times of polyolefin fine porous membrane.

[0035]

[Example]Although this invention is concretely explained below based on an example, this invention is not limited at all by these examples. The measurement in an example and a comparative example depended on the following method.

[0036][1. Average pore size] of a porous body The figure was made into the average pore size, after having observed the surface of the enveloping layer used as a specimen by one 500 times the magnification of this with the scanning electron microscope (SEM), measuring the interval of ten openings at random and calculating those average value.

[0037][-- 2. -- air permeability] -- it measured based on JIS P8117. (Unit: sec/100cc)

[0038]Example 1 - 4 polyethylene fine porous membrane (the Tonen Chemical make and 23.5 micrometers of thickness) 0.03 micrometer of average pore sizes, 0.05 micrometer in the maximum aperture, 38% of a void content, 878 sec of air permeability/100cc is stuck on a glass plate, using a control coating machine at a room temperature -- polyvinylidene fluoride (the Kureha Chemical Industry

[Co., Ltd.] Co., Ltd. make.) Trade name: After applying on condition of as N-methyl-pyrrolidone solution of KF polymer #1120 was indicated to the following table 1, being immersed in ethanol at the room temperature and being air-dry at the room temperature subsequently, it dried with 80 ** air oven. When the polyvinylidene fluoride enveloping layer formed on the obtained bipolar membrane was observed with 5000 times as many scanning electron microscopes (SEM), as shown in drawing 1, it has checked that it was the sparse porous structure which consists of several micrometer a unit of opening which rod-like edge connected. When the thickness of the obtained bipolar membrane, the average pore size of an enveloping layer, and the air permeability of bipolar membrane were measured, it was as being shown in the following table 1.

[0039]Comparative example 1 polyethylene fine porous membrane (the Tonen Chemical make and 23.5 micrometers of thickness) 0.03 micrometer of average pore sizes, 0.05 micrometer in the maximum aperture, 38% of a void content, 878 sec of air permeability/100cc is stuck on a glass plate, After applying the 10-% of the weight acetone solution of polyvinylidene fluoride (Kureha Chemical Industry [Co., Ltd.] Co., Ltd. make and trade name:KF polymer #1300) to a thickness of 75 micrometers using a control coating machine at a room temperature and it was air-dry at the room temperature, it dried with 80 ** air oven. Porous structure was not checked when the polyvinylidene fluoride enveloping layer formed on the obtained bipolar membrane was observed with 5000 times as many scanning electron microscopes (SEM). Although the thickness of the obtained bipolar membrane was 33.5 micrometers, air permeability is incapable measurement and effective permeability was not accepted.

[0040]

[Table 1]

	PVDF溶液	塗布厚さ μ m	膜厚 μ m	平均孔径 μ m	透気度 秒/百cc
実施例 1	2 倍希釈	1 0	2 5 . 4	4	9 5 0
実施例 2	原液	2 5	2 7 . 6	2 . 5	1 3 9 3
実施例 3	原液	7 5	3 2 . 3	2 . 5	1 4 3 4
実施例 4	原液	1 7 5	4 2 . 0	2 . 5	1 6 6 6

[0041]As shown in the above-mentioned table 1, in the bipolar membrane of this invention obtained in Examples 1-4. The average pore size of a coating layer is larger than the maximum aperture of polyethylene fine porous membrane, as a result to air permeability being stopped 1.08 to 1.9 times of the air permeability of polyethylene fine porous membrane, by the comparative example, a hole is not substantially observed by the coating layer but permeability is barred. According to the bipolar membrane of this invention, this shows easily that functionality can be granted, without barring permeability greatly.

[0042]

[Effect of the Invention]In this invention, in the bipolar membrane which forms the enveloping layer which consists of a porous body of a functional polymer substance gelable to the 1st [at least] page of polyolefin fine porous membrane, the average pore size of a porous body is adjusted so that it may become larger than the maximum aperture of polyolefin fine porous membrane.

Therefore, in the field of a chemical cell like a lithium cell. Gap between the members forming in the electrolysis solution pouring nature in a battery construction process, or repetition charge and discharge, There is no inconvenience by a crevice etc. and it can be used as a very quality separator which interfacial resistance can also reduce, Wettability with the drug solution which furthermore serves as a candidate for separation also in the field of a demarcation membrane is good, therefore the bipolar membrane which can be used as a barrier filter in which filtration velocity etc. have been improved remarkably is obtained, and the industrial value is very large.